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Modified Rocard Relation for Complex Permittivity

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Synopsis

It is shown that to a high degree of accuracy the complex permittivity for a gas dielectric or for a liquid dielectric in very dilute solution in a nonpolar solvent is given theoretically for symmetric polar molecules by the modification of a relation, which essentially goes back to Rocard. When the molecules are linear or spherical, the modified relation is particularly simple. There is no simple relation for complex permittivity when the polar molecules are asymmetric. Thus in comparing the theory of rotational Brownian motion with the results of dielectric relaxation experiments it would seem advisable at the present stage to focus attention on experiments performed with symmetric polar molecules, preferably spherical or linear.

The complex relative permittivity $\varepsilon(\omega)$ for a gas dielectric or for a very dilute solution of a liquid dielectric in a nonpolar solvent is given by the Kubo equation[1]

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = 1 - i\omega \int_0^\infty \langle (\underset{\sim}{n}(0) . \underset{\sim}{n}(t)) \rangle e^{-i\omega t} dt, \qquad (1)$$

where ε_s is the static relative permittivity, ε_∞ is the relative permittivity for frequencies so high that dipolar polarization is no longer effective, $\underset{\sim}{n}(t)$ is a unit vector in the direction of the dipole moment of a molecule of the dielectric and the angular brackets denote ensemble average. The relative permittivity $\varepsilon'(\omega)$ and the loss factor $\varepsilon''(\omega)$ are related to $\varepsilon(\omega)$ by

$$\varepsilon(\omega) = \varepsilon'(\omega) - i\varepsilon''(\omega).$$

If $R(t)$ is the stochastic rotation operator[2] that brings axes fixed in the molecule from their orientation at time zero to their orientation at time t, it is easy to see that

$$(n(0) . n(t)) = R'_{00}(t),$$

the 00 -element of R(t) in the three-dimensional representation having as basis vectors the spherical harmonics $Y_{1,-1}, Y_{1,0}, Y_{1,1}$. Hence eq. (1) is expressible as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = 1 - i\omega \int_0^\infty \langle R(t) \rangle'_{00} e^{-i\omega t} dt \qquad (2)$$

In order to calculate the complex permittivity from this equation it is necessary to express $\langle R(t) \rangle$ in a way that will allow the integration in (2) to be performed. Let us first take the case where each polar molecule may be regarded as a sphere with moment of inertia I about a diameter, and let us suppose that in the thermal motion a frictional couple of moment IB times the

angular velocity acts on the molecule. It has been found [3], when inertial effects are included in the calculation, that

$$\begin{aligned}\langle R(t)\rangle = \Big[\underset{\approx}{I} &+\gamma J^2(1-e^{-Bt}) + \gamma^2\Big\{J^2\Big[\tfrac{5}{4}-(Bt+1)e^{-Bt}-\tfrac{1}{4}e^{-2Bt}\Big] \\ &+(J^2)^2\Big[\tfrac{1}{2}-e^{-Bt}+\tfrac{1}{2}e^{-2Bt}\Big]\Big\} \\ &+\gamma^3\Big\{J^2\Big[\tfrac{19}{9}-(\tfrac{1}{2}B^2t^2+2Bt+1)e^{-Bt}-(\tfrac{3}{4}Bt+1)e^{-2Bt}-\tfrac{1}{9}e^{-3Bt}\Big] \\ &+(J^2)^2\Big[\tfrac{5}{4}-(Bt+\tfrac{9}{4})e^{-Bt}+(Bt+\tfrac{3}{4})e^{-2Bt}+\tfrac{1}{4}e^{-3Bt}\Big] \\ &+(J^2)^3\Big[\tfrac{1}{6}-\tfrac{1}{2}e^{-Bt}+\tfrac{1}{2}e^{-2Bt}-\tfrac{1}{6}e^{-3Bt}\Big]\Big\}+\cdots\Big] \\ &\times \exp\Big[-\gamma B\{1+\tfrac{1}{2}\gamma+\tfrac{7}{12}\gamma^2+(\tfrac{17}{18}-\tfrac{1}{8}J^2)\gamma^3+\cdots\}J^2t\Big],\end{aligned} \tag{3}$$

where $\underset{\approx}{I}$ is the identity operator, J^2 is the square of the rotation operator (J_x, J_y, J_z) and $\gamma = kT/(IB^2)$, a small dimensionless quantity whose order for magnitude is 0.01. The value of $\langle R(t)\rangle'_{OD}$ is obtained from (3) on replacing $\underset{\approx}{I}$ by unity and J^2 by 2 in the right hand side. When this value is substituted into (2), we deduce that

$$\begin{aligned}\frac{\xi(\omega)-\xi_\infty}{\xi_s-\xi_\infty} = \frac{G'}{G'+i\omega'} - i\omega'\Big\{&\gamma\Big[\frac{2}{G'+i\omega'}-\frac{2}{1+G'+i\omega'}\Big] \\ &+\gamma^2\Big[\frac{\frac{9}{2}}{G'+i\omega'}-\frac{6}{1+G'+i\omega'}-\frac{2}{(1+G'+i\omega')^2}+\frac{\frac{3}{2}}{2+G'+i\omega'}\Big] \\ &+\gamma^3\Big[\frac{\frac{95}{9}}{G'+i\omega'}-\frac{15}{1+G'+i\omega'}-\frac{8}{(1+G'+i\omega')^2}-\frac{2}{(1+G'+i\omega')^3} \\ &+\frac{5}{2G'+i\omega'}+\frac{\frac{5}{2}}{(2+G'+i\omega')^2}-\frac{\frac{5}{9}}{3+G'+i\omega'}\Big]+\cdots\Big\},\end{aligned} \tag{4}$$

where

$$\begin{aligned}G' &= 2\gamma(1+\tfrac{1}{2}\gamma+\tfrac{7}{12}\gamma^2+\tfrac{25}{36}\gamma^3+\cdots) \\ \omega' &= \frac{\omega}{B}.\end{aligned} \tag{5}$$

When $\omega' \ll 1$, the sums in the square brackets of (4) are of the order of magnitude of their first terms. When $\omega' = 1$, the order of magnitude of all the sums is unity. When $\omega' \gg 1$, the sums are all of order ω'^{-2} . It therefore seems reasonable to suppose for all values of ω' that the terms in the braces with ascending powers of γ are progressively smaller and that each such term is of order of magnitude γ relative to the preceding one. We now agree to omit the terms proportional to $\gamma^2, \gamma^3, \ldots$, thus obtaining

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{G'(1 + G' + i\omega') - 2\gamma i\omega'}{(G' + i\omega')(1 + G' + i\omega')}$$

$$= \frac{G'(1 + G') + \gamma^2 i\omega'}{(G' + i\omega')(1 + G' + i\omega')}$$

from (5) on neglecting higher order terms in G' . Hence in this approximation

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1 + \dfrac{\gamma^2 i\omega'}{G'(1 + G')}}{\left(1 + \dfrac{i\omega'}{G'}\right)\left(1 + \dfrac{i\omega'}{1 + G'}\right)} . \qquad (6)$$

To put this into a form that would be more suitable for comparison with dielectric experiments we define a friction time τ_F as $\mathcal{B}^{-1}$, so that $\omega' = \omega\tau_F$, and we write

$$\frac{I\mathcal{B}}{2kT} = \tau_D ,$$

the relaxation time that occurs in the Debye theory[4]. We note that

$$\tau_F = 2\gamma\tau_D = \frac{I}{2kT\tau_D} . \qquad (7)$$

Then we deduce on employing (5) that approximately

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1 + \frac{1}{2}\gamma i\omega\tau_F}{\left(1 + i\omega\left[\tau_D - \frac{1}{4}\tau_F\right]\right)\left(1 + i\omega\tau_F[1 - 2\gamma]\right)} . \qquad (8)$$

It is found in experiments on dielectric relaxation [5], that $\gamma \omega \tau_F$ is of order of magnitude unity only for frequencies well above the range of validity of the classical statistical mechanics which has been employed in the derivation of (8). Hence for consistency we do not consider such frequencies, and so we replace (8) by

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{\left(1 + i\omega\left[\tau_D - \tfrac{1}{4}\tau_F\right]\right)\left(1 + i\omega\tau_F\right)} . \tag{9}$$

In a different but equivalent study of inertial effects on orientational polarization [6] a relation was obtained that may be expressed in the present context as

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{G'(1+G')}{(G'+i\omega')(1+G'+i\omega')} - \frac{i\omega' G'^2\left\{\frac{5}{4}(G'+i\omega') + \frac{7}{4}\right\}}{(G'+i\omega')(1+G'+i\omega')^2(2+G'+i\omega')} - \cdots .$$

If the series on the right hand side is truncated after the first term and if we neglect quantities proportional to $\gamma \omega \tau_F$, we again obtain (9).

Rocard [7] investigated the effect of the inertia of polar spherical molecules on orientational polarization. His investigations were inadequate, since they were based on a Brownian motion differential equation which does not exist. However, he deduced a result for polarizability which in our notation would be obtained by taking real parts in the equation

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{(1 + i\omega\tau_D)(1 + i\omega\tau_F)} . \tag{10}$$

We shall refer to this as the Rocard relation. We may regard (9) as providing a correction to (10); eq. (9) is a modified Rocard relation.

When the polar molecule is a linear rotator, (3) is replaced by [3]

$$\langle R(t)\rangle = \left[\underline{\underline{I}}_m + \gamma J^2(1-e^{-Bt}) + \gamma^2\left\{J^2\left[\tfrac{5}{2} - (2Bt+2)e^{-Bt} - \tfrac{1}{2}e^{-2Bt}\right] + (J^2)^2\left[\tfrac{1}{2} - e^{-Bt} + \tfrac{1}{2}e^{-2Bt}\right]\right\} + \cdots\right] \times \exp\left[-\gamma B(1+\gamma + \tfrac{8}{3}\gamma^2 + \ldots) J^2 t\right].$$

It will then follow that

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty} = \frac{G''}{G''+i\omega'} - i\omega'\left\{\gamma\left[\frac{2}{G''+i\omega'} - \frac{2}{1+G''+i\omega'}\right] + \gamma^2\left[\frac{7}{G''+i\omega'} - \frac{8}{1+G''+i\omega'} - \frac{4}{(1+G''+i\omega')^2} + \frac{1}{2+G''+i\omega'}\right] + \cdots\right\}$$

with

$$G'' = 2\gamma(1+\gamma+\tfrac{8}{3}\gamma^2+\ldots).$$

Proceeding as above for the sphere we obtain

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty} = \frac{1}{(1+i\omega[\tau_D - \frac{1}{2}\tau_F])(1+i\omega\tau_F)} \qquad (11)$$

in place of (9). Equation (11) is the modified Rocard relation for the linear rotator.

We next consider the case of an asymmetric polar molecule. An expression for the complex polarizability due to the rotational Brownian motion of asymmetric polar molecules has been given by Ford, Lewis and McConnell [8]. Neglecting terms that are of significance only for frequencies in the quantum region we may write

$$\frac{\varepsilon(\omega)-\varepsilon_\infty}{\varepsilon_s-\varepsilon_\infty} = \frac{n_1^2}{D_2+D_3+i\omega}\left\{\frac{D_2(D_2+D_3+B_2)}{D_2+D_3+B_2+i\omega} + \frac{D_3(D_2+D_3+B_3)}{D_2+D_3+B_3+i\omega}\right\} + \frac{n_2^2}{D_3+D_1+i\omega}\left\{\frac{D_3(D_3+D_1+B_3)}{D_3+D_1+B_3+i\omega} + \frac{D_1(D_3+D_1+B_1)}{D_3+D_1+B_1+i\omega}\right\} + \frac{n_3^2}{D_1+D_2+i\omega}\left\{\frac{D_1(D_1+D_2+B_1)}{D_1+D_2+B_1+i\omega} + \frac{D_2(D_1+D_2+B_2)}{D_1+D_2+B_2+i\omega}\right\}. \qquad (12)$$

Coordinate axes labelled 1, 2, 3 have been taken through the centre of mass and in the directions of the principal axes of inertia, the corresponding moments of inertia being I_1, I_2, I_3 . The moment about the ith axis of the frictional couple is supposed to be $I_i B_i$ times the ith component of the angular velocity of the molecule. The direction cosines of the dipole axis are n_1 , n_2 , n_3 ,

$$D_1 = D_1^{(1)} + D_1^{(2)} \tag{13}$$

$$D_1^{(1)} = \frac{kT}{I_1 B_1} \tag{14}$$

$$D_1^{(2)} = \frac{(kT)^2}{I_1 I_2 I_3}\left[I_1 \frac{2B_2B_3(B_2+B_3) - B_1(B_2^2+B_2B_3+B_3^2)}{B_1 B_2^2 B_3^2 (B_2+B_3)} \right.$$

$$+ I_2 \frac{B_2(B_2+B_3)-2B_3^2}{B_1 B_2 B_3^2 (B_2+B_3)} + I_3 \frac{B_3(B_2+B_3)-2B_2^2}{B_1 B_2^2 B_3 (B_2+B_3)} \tag{15}$$

$$\left. - \frac{(I_2-I_3)^2}{I_1 B_1^2 (B_2+B_3)} \right], \text{ etc.}$$

It is seen that $D_i^{(2)}$ is a small correction to $D_i^{(1)}$ of relative order $kT/(IB^2)$, where I and B denote generic values of the moments of inertia and frictional constants. Equation (12) has not the structure of a modified Rocard relation.

We next specialize to the case where the polar molecule has an axis of symmetry, which we choose to be the third coordinate axis. On account of the symmetry the dipole lies along the third axis and we put

$$n_1 = n_2 = 0 , n_3 = 1 , I_2 = I_1, B_2 = B_1.$$

Hence (12) reduces to

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{2D_1(2D_1 + B_1)}{(2D_1 + i\omega)(2D_1 + B_1 + i\omega)} \tag{16}$$

$$= \frac{1}{\left(1 + \frac{i\omega}{2D_1}\right)\left(1 + \frac{i\omega}{B_1 + 2D_1}\right)},$$

where D_1 is given by (13), $D_1^{(1)}$ by (14), and (15) becomes

$$D_1^{(2)} = \frac{(kT)^2}{I_1^2 I_3}\left[I_1 \frac{2B_1 - B_3}{B_1^2 B_3 (B_1 + B_3)} + I_3 \frac{-2B_1^2 + B_1 B_3 + B_3^2}{B_1^3 B_3 (B_1 + B_3)} - \frac{(I_1 - I_3)^2}{I_1 B_1^2 (B_1 + B_3)}\right] \quad (17)$$

In eqn (16) we have

$$\frac{\omega}{2D_1} = \frac{\omega}{2D_1^{(1)}\left(1 + \frac{D_1^{(2)}}{D_1^{(1)}}\right)} = \omega\tau_D\left(1 - \frac{D_1^{(2)}}{D_1^{(1)}}\right)$$

approximately, where we have put $I_1 B_1/(2kT)$ equal to τ_D. Moreover

$$B_1 + 2D_1 = B_1\left(1 + 2\gamma\left[1 + \frac{D_1^{(2)}}{D_1^{(1)}}\right]\right)$$

with $\gamma = kT/(I_1 B_1^2)$. Then on writing $B_1^{-1} = \tau_F$,

$$\frac{\omega}{B_1 + 2D_1} = \omega\tau_F\left(1 - 2\gamma\left[1 + \frac{D_1^{(2)}}{D_1^{(1)}}\right]\right) = \omega\tau_F,$$

since we may neglect the term proportional to γ because it is insignificant for values of ω belonging to the range of validity of classical statistical mechanics. We conclude that

$$\frac{\varepsilon(\omega) - \varepsilon_\infty}{\varepsilon_s - \varepsilon_\infty} = \frac{1}{\left(1 + i\omega\tau_D\left[1 - \frac{D_1^{(2)}}{D_1^{(1)}}\right]\right)(1 + i\omega\tau_F)} \quad (18)$$

with $D_1^{(1)}$ and $D_1^{(2)}$ given by (14) and (17). This is the modified Rocard relation for the symmetric rotator.

In the course of the derivation of (12) for the asymmetric rotator certain approximations were made. We shall now consider whether these approximations, at least when employed for the symmetric rotator, are consistent with our treatment of the spherical and linear rotators. For this purpose we examine whether (18) reduces to (9) and (11) for the sphere and linear rotator, respectively.

The case of the sphere presents no difficulty. It is seen immediately from (14) and (17) that for $I_1 = I_3 = I$, $B_1 = B_3 = B$

$$\frac{\tau_D D_1^{(2)}}{D_1^{(1)}} = \frac{\tau_D kT}{2IB^2} = \frac{1}{4}\tau_F ,$$

by (7). This is what we require for (9). The case of the linear rotator needs more careful consideration. We have from (14) and (17)

$$\frac{D_1^{(2)}}{D_1^{(1)}} = \frac{kT}{I_1 B_1^2} \frac{\frac{2I_1}{I_3}\left(\frac{B_1^2}{B_3^2} - \frac{B_1}{B_3}\right) - \frac{2B_1^2}{B_3^2} + \frac{3B_1}{B_3} + 1 - \frac{I_3 B_1}{I_1 B_3}}{1 + \frac{B_1}{B_3}} . \qquad (19)$$

For the linear rotator $I_3 \ll I_1$ and, if in addition we require that $B_3 \gg B_1$ in such a way that $I_3 B_3 \gg I_1 B_1$, we deduce from (19) that

$$\frac{D_1^{(2)}}{D_1^{(1)}} = \frac{kT}{I_1 B_1^2} .$$

Then on substituting into (18) we shall obtain (11). It is therefore possible to define a limiting process that will lead from the modified Rocard relation for the symmetric rotator to that for the linear rotator.

The first result of the foregoing investigations is that, when a dielectric consists of polar molecules with an axis of symmetry, the complex permittivity is given to a first approximation by the Rocard relation (10). This equation has the advantage that its right hand side involves only one frictional parameter τ_F, which is deducible from τ_D by (7). The value of τ_D may often be obtained from an experimental Cole-Cole plot. To a

second approximation the permittivity is given by a modified Rocard relation, which in the cases of spherical and linear rotators assumes the simple forms (9) and (11) having only the one frictional parameter τ_F but in the general case is given by (18) and so involves two frictional constants $\mathcal{B}_1$ and $\mathcal{B}_3$. This would make difficult the comparison of theoretical and experimental results for the relativity permittivity $\varepsilon'(\omega)$ and the loss factor $\varepsilon''(\omega)$. Since eq. (12) involves the frictional constants $\mathcal{B}_1, \mathcal{B}_2, \mathcal{B}_3$ and since there are no obvious ways of determining the values of these, either experimentally or theoretically, it seems that we cannot hope at present to institute accurate comparisons between theoretical and experimental values of $\varepsilon'(\omega)$ and $\varepsilon''(\omega)$ for dielectrics composed of asymmetric polar molecules.

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